A mechanistic study on photocatalysis by thiapyrylium salts. Photodegradation of dimethoate, alachlor and pyrimethanil under simulated sunlight

J. Gomis [a], A. Arques [a], A.M. Amat [a], M.L. Marin [b], M.A. Miranda [b],*

[a] Grupo de Procesos de Oxidación Avanzada, Departamento de Ingeniería Textil y Papelera, Universidad Politécnica de Valencia, Campus de Alcoy, Plaza Ferrándiz y Carbonell, E-03801, Alcoy, Spain
[b] Instituto Universitario Mixto de Tecnología Química (UPV-CSIC)-Departamento de Química, Avda. de los Naranjos s/n, E-46022, Valencia, Spain

ABSTRACT

Photodegradation of dimethoate, alachlor, and pyrimethanil using a thiapyrilium salt (TPTP$^+$) as photocatalyst was performed under simulated sunlight. The photocatalyst removes preferentially pyrimethanil (45% after 60 min of irradiation), followed by dimethoate (20%) and alachlor (13%). In the three cases, an important to moderate decrease of the fluorescence intensity upon addition of the pollutants was observed. The active participation of the singlet excited state in the photodegradation of the pollutants was demonstrated; the corresponding dynamic quenching rate constants were found to be 1.9×10^{10} M^{-1} s^{-1} (pyrimethanil), 6.7×10^9 M^{-1} s^{-1} (dimethoate) and 9.1×10^9 M^{-1} s^{-1} (alachlor). Moreover, a decrease in the signal corresponding to the triplet excited state was observed immediately after the laser pulse; again a good correlation was observed between the missing fraction of triplets and the photodegradation rates under solar light. Detection of TPTP$^+$, the reduced species derived from the photocatalyst, as well as Rehm–Weller calculations on the free energy changes, strongly support an electron transfer mechanism occurring from the singlet excited state.

© 2012 Published by Elsevier B.V.

1. Introduction

Solar-driven photochemical oxidation of pollutants using organic photocatalysts has deserved considerable attention in recent years [1,2]. One of the main advantages of organic photocatalysts is their intense absorption in the UVA-visible region of the spectrum. In addition, they operate through a variety of photochemical mechanisms, from direct electron transfer to the generation of reactive oxygen species, providing a versatile tool for optimizing the efficiency of photocatalytic processes [3,4]. In this context, mechanistic studies including detection of transient species and identification of intermediates are essential to assess the viability of photochemical remediation [5].

In fact, an intensive effort has been devoted during the last decade to evaluate the potential of organic photocatalysts for the decontamination of toxic effluents, as an alternative to the established advanced oxidation processes [2]. Thus, removal of phenols [6–8], pesticides [9–11] or even warfare agents [12] has been achieved following this methodology. In general, the stability and possibility of re-use are substantially enhanced by adsorption onto solid supports [13–15].

Pyrylium and thiapyrylium salts are well known organic photocatalysts acting mainly via an electron-transfer mechanism [3]. They have shown a marked photooxidizing ability in homogeneous phase [8,11,16,17], as well as hosted in different materials, such as zeolites [12,18,19], silica gel [20] or sepiolites [21–23].

With this background, the aim of the present work is to elucidate the mechanistic pathways involved in the 2,4,6-triphenylthiapyrylium (TPTP$^+$)-mediated photodegradation of dimethoate, alachlor and pyrimethanil (see Fig. 1), because they are commonly employed pesticides having different chemical structures; hence, they can be chosen as model pollutants. Interestingly, a good correlation has been found between the photophysical properties and the removal efficiency under simulated sunlight.

2. Experimental

2.1. Chemicals

Dimethoate, alachlor, pyrimethanil and 2-amino-4,6-dimethylpyrimidine were supplied by Aldrich (Pestanal); 2,4,6-triphenylthiapyrylium perchlorate was obtained according to the procedure previously described [24]. Briefly, an aqueous solution of sodium sulfide (10% w/w) was added to a solution of 0.17 g of 2,4,6-triphenylpyrylium tetrafluoroborate (Aldrich) in
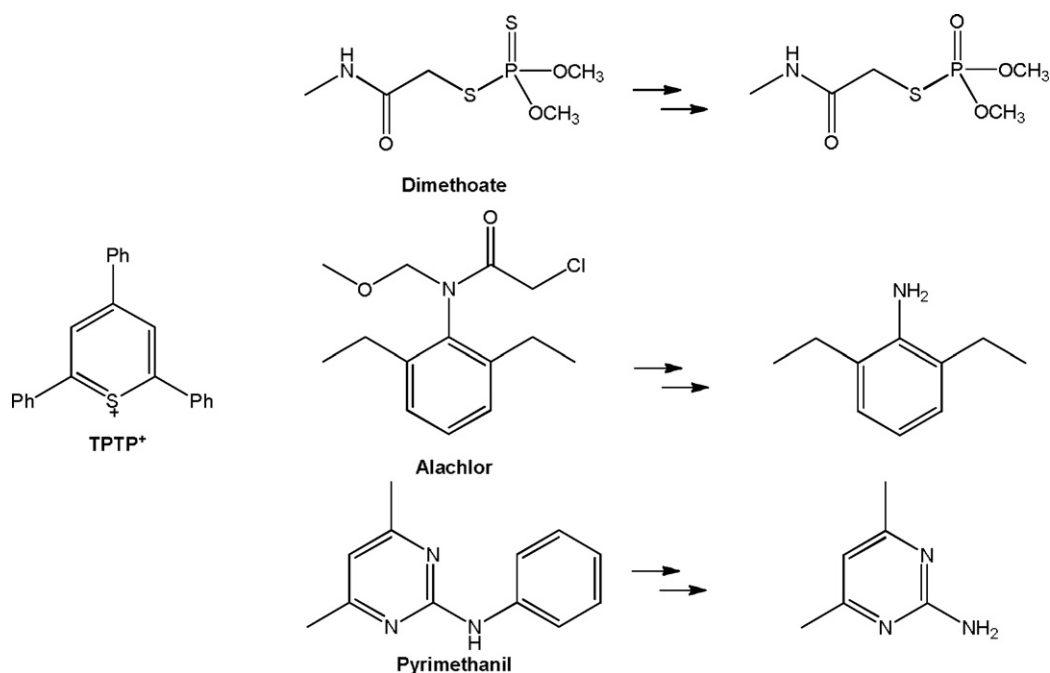
Fig. 1. Chemical structures of the thiapyrylium cation, the selected pesticides and the corresponding major photodegradation products.

8 ml of acetone, until the mixture turned red. Then, the crude was acidified with perchloric acid (20% w/w) and diluted with water (8 ml). The 2,4,6-triphenylthiapyrylium perchlorate, obtained as a yellow powder was filtered and purified by recrystallization.

Acetonitrile, used as solvent for photophysical experiments, was of HPLC quality from Merck. Water used in photophysical and photochemical experiments was deionized milli-Q® (Millipore, Bedford, MA, USA).

2.2. Solar simulated reactions

Irradiations were performed in open glass vessels, loaded with 250 ml of an aqueous solution of the mixture of the three pesticides (initial concentration: 50 mg/l each) and the photocatalyst (10 mg/l). In order to prevent hydrolysis of the latter at neutral or basic media [20] the pH of the solution was adjusted to 3 by adding hydrochloric acid. Samples were irradiated by means of a solar simulator (Oriel Instruments, Model 81160 equipped with a 300 W Xenon lamp). Magnetic stirring was kept all along the reaction time, and water was added periodically in order to compensate for the evaporation loss.

Concentration of the pesticides was determined by liquid chromatography. Aliquots taken from the reaction mixture were filtered through polypropylene (0.45 μm) and then injected into the HPLC (PerkinElmer Autosystem XL). A LiChrosphere 100 RP-18 column was employed, and the eluent was an isocratic mixture of acetonitrile (50%) and water (50%). UV-Detection was fixed at 210 nm.

For the identification of the major photoproducts, aliquots obtained at the end of the irradiation were submitted to GC–MS or HPLC–MS analysis. Before injection into GC–MS (Shimadzu QP2010S, with quadrupole mass analyzer), samples were preconcentrated by solid phase extraction (SPE). Briefly, different aliquots of the sample (50 ml) were adjusted to pH of 3, then they were flown through a LiChrolut EN 200 mg (Merck) cartridge; the products were recovered with 3 ml of methanol. The injector temperature was 250 °C, and the split ratio was 1:30. A Meta X5 Teknokroma column was used with helium as carrier gas, with a flow rate of 35 ml/min. The column temperature was kept at 60 °C for 3 min,

then it was increased with a 8 °C/min rate from 60 °C to 280 °C and finally it was kept at 280 °C for 3 min.

For the HPLC–MS a 1100 Series LC/MSD Agilent instrument with API-ES positive ionization for mass detection was used. Aliquots taken at the final reaction times were filtered through polypropylene (0.45 μm) and then injected. A Mediterranea Sea C18 column (5 μm) was employed, and the eluent was an isocratic mixture of acetonitrile (75%) and aqueous trifluoroacetic acid (25%). UV-Detection was fixed at 210 nm.

2.3. Photophysical measurements

Quartz cells of 1 cm optical path length were employed for all photophysical measurements, which were run in degassed acetonitrile at room temperature.

Absorption spectra were taken with a double beam Cary 300 UV–vis spectrophotometer (UV0811M209, Varian). Fluorescence spectra were recorded on a FS900 fluorometer. The absorbance of solutions at the excitation wavelength (420 nm) was kept below 0.1. Fluorescence lifetime measurements were based on single-photon-counting using a hydrogen flashlamp (1.5 ns pulse width) as excitation source. For the static or dynamic fluorescence quenching experiments, increasing amounts of the pollutant (in the range 1.6×10^{-4} to 1.5×10^{-2} M) were added to the corresponding TPTP$^+$ solution in deaerated acetonitrile.

Laser flash photolysis studies were carried out with a Nd:YAG SL404G-10 spectron laser systems using 355 nm as the excitation wavelength. The single pulses were of ca. 10 ns duration, and the energy was lower than 20 mJ per pulse. The detecting light source was a pulsed Lo255 Oriel Xenon lamp. The laser flash photolysis system consisted of the pulsed laser, the Xe lamp, a 77200 Oriel monochromator, a photomultiplier (Oriel, model 70705) system and a TDS-640A Tektronix oscilloscope. The output signal from the oscilloscope was transferred to a personal computer. Deaerated acetonitrile solutions of TPTP$^+$ (7×10^{-5} M) in the presence of increasing amounts of the pollutants (up to 1.6×10^{-4} M) were used in the laser flash photolysis experiments.
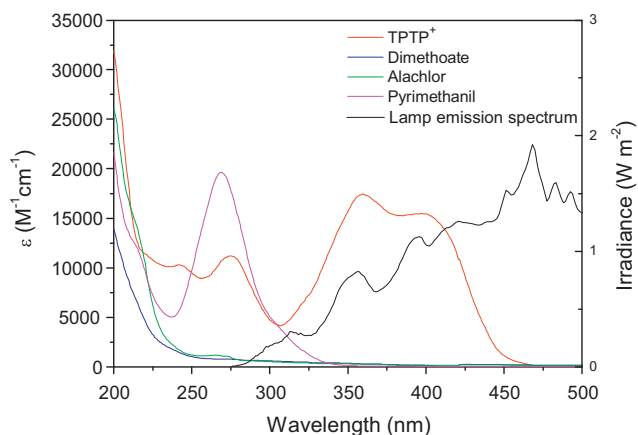
Fig. 2. Overlap of the absorption spectra of TPTP+, dimethoate, alachlor and pyrimethanil with the emission of the solar simulator.

3. Results and discussion

3.1. Solar simulated photodegradation of the pesticides

First, the absorption spectra of all three pesticides and the photocatalyst were obtained and plotted *vs.* the emission of the solar simulator (Fig. 2). There was an important overlap between the emission of the lamp and the absorption of TPTP+, in particular in the wavelength range from 300 to 450 nm. In the case of the pollutants, although some overlap was indeed found, it was comparatively very low. However, in order to determine the extent of direct photolysis of the pollutants, they were irradiated in the absence of TPTP+; no significant degradation was observed after 60 min.

Then, photolysis of the three pesticides in the presence of TPTP+ was performed under simulated sunlight. Data show (Fig. 3) that the photocatalyst removes preferentially pyrimethanil, as 45% of this pollutant disappeared after 60 min of irradiation. Some photodegradation of the two other pesticides was also observed, although to a considerably lower extent: 20% and 13% for dimethoate and alachlor, respectively. This trend is opposite to that recently reported for the photo-Fenton and TiO$_2$-based treatments, indicating that pyrimethanil is more reluctant to photo-oxidation than dimethoate or alachlor [23]. On the other hand, the same qualitative pattern as for TPTP+ is observed with 2,4,6-triphenylpyrylium cation (TPP+) as photocatalyst [23]. This has been attributed to differences in the reaction mechanisms. Thus, in the TiO$_2$ and photo-Fenton processes, where
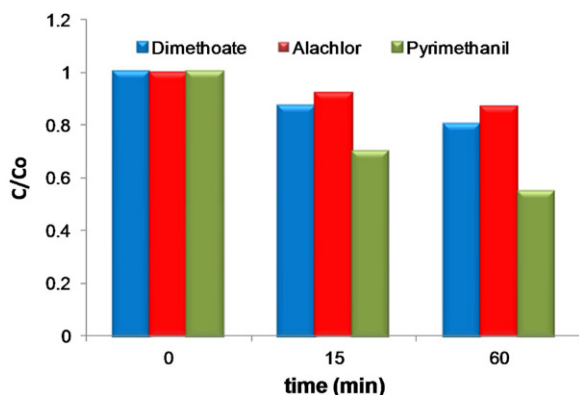

Fig. 3. Plot of the relative concentrations of the remaining pesticides ($C_i = 50$ mg/l, each) after simulated sunlight irradiation in the presence of TPTP+ (10 mg/l).

hydroxyl radical plays an important role, faster reaction rates are measured for dimethoate or alachlor than for pyrimethanil. Conversely, in the TPP+-mediated reaction a more complex mechanism has been proposed involving electron transfer within a non-emissive ground state complex [23].

Upon prolonged irradiation a considerable decrease in the reaction rate was observed; this effect has been previously observed in the TPP+ or TPTP+-photocatalyzed reactions in aqueous media [2,11,15] and is attributable to partial solvolysis of the heterocyclic ring [20]. However, this is not a major drawback for practical purposes, as in general (thia)pyrilium salts are employed in homogeneous phase only for mechanistic studies, while they are preferentially adsorbed onto inorganic supports for real applications in wastewater detoxification [2].

Furthermore, detailed CG–MS and HPLC–MS analysis of the irradiation mixtures was performed. The main photoproducts found indicated substitution of sulfur by oxygen in the case of dimethoate, diethylaniline as the major fragment derived from alachlor and 2-amino-4,6-dimethylpyrimidine as the major photoproduct of pyrimethanil (Fig. 1) [25,26].
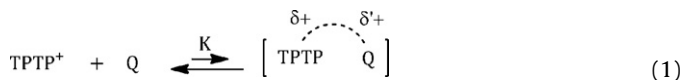
3.2. Photophysical studies

Systematic photophysical studies were carried out in order to establish the mechanism operating in the TPTP+-photocatalyzed degradation of dimethoate, alachlor and pyrimethanil. Specifically, the involvement of a photochemical electron transfer mechanism between the excited states (singlet and/or triplet) of TPTP+ and the pesticides, as well as formation of ground-state complexes, was analyzed.

3.2.1. Emission

First, the possible participation of the TPTP+ singlet excited state in the photodegradation mechanism was investigated. Thus, when the fluorescence spectrum of TPTP+ in deaerated acetonitrile (with a maximum at 458 nm) [22] was recorded in the presence of increasing amounts of the pollutants, a decrease of the emission intensity was observed in every case (Fig. 4A, C and E).

Then, the active participation of the singlet state in the photodegradation of the pollutants was also investigated. Thus, when the fluorescence quenching was studied by means of time-resolved emission spectroscopy, a decrease of the singlet TPTP+ lifetimes with increasing concentrations of the pollutants was observed in every case. From the Stern–Volmer plots (Fig. 4B, D and F, solid symbols), the corresponding rate constants were found to be 9.1×10^9, 6.7×10^9 and 1.9×10^{10} M^{-1} s^{-1} for dimethoate, alachlor and pyrimethanil, respectively.

In general, the relative changes in the steady-state emission intensity deviated clearly from the linear relationships (Fig. 4B, D and F, open symbols) found for the dynamic quenching, pointing to the formation of non-emissive ground-state complexes (Eq. (1)). This effect was especially noticeable in the case of pyrimethanil.

$$\text{TPTP}^+ + Q \xrightleftharpoons{K} \left[\overset{\delta+}{\text{TPTP}} \cdots \overset{\delta'+}{Q} \right] \qquad (1)$$

Assuming that the Benesi and Hildebrand [27,28] relationship applies in these cases, rough estimations were made on the extent of complexation between the pollutants and TPTP+, for 1:1 stoichiometry. Equilibrium constants in the order of 10^2 M^{-1} were obtained, indicating that the amount of complex at the pollutant concentrations typical of the solar simulated experiments ($1.8–2.5 \times 10^{-4}$ M) was very low (less than 1%).

Accordingly, when the dynamic quenching constant (k_q) was plotted *versus* the degradation percentage under simulated solar irradiation for the three pesticides a good correlation was found
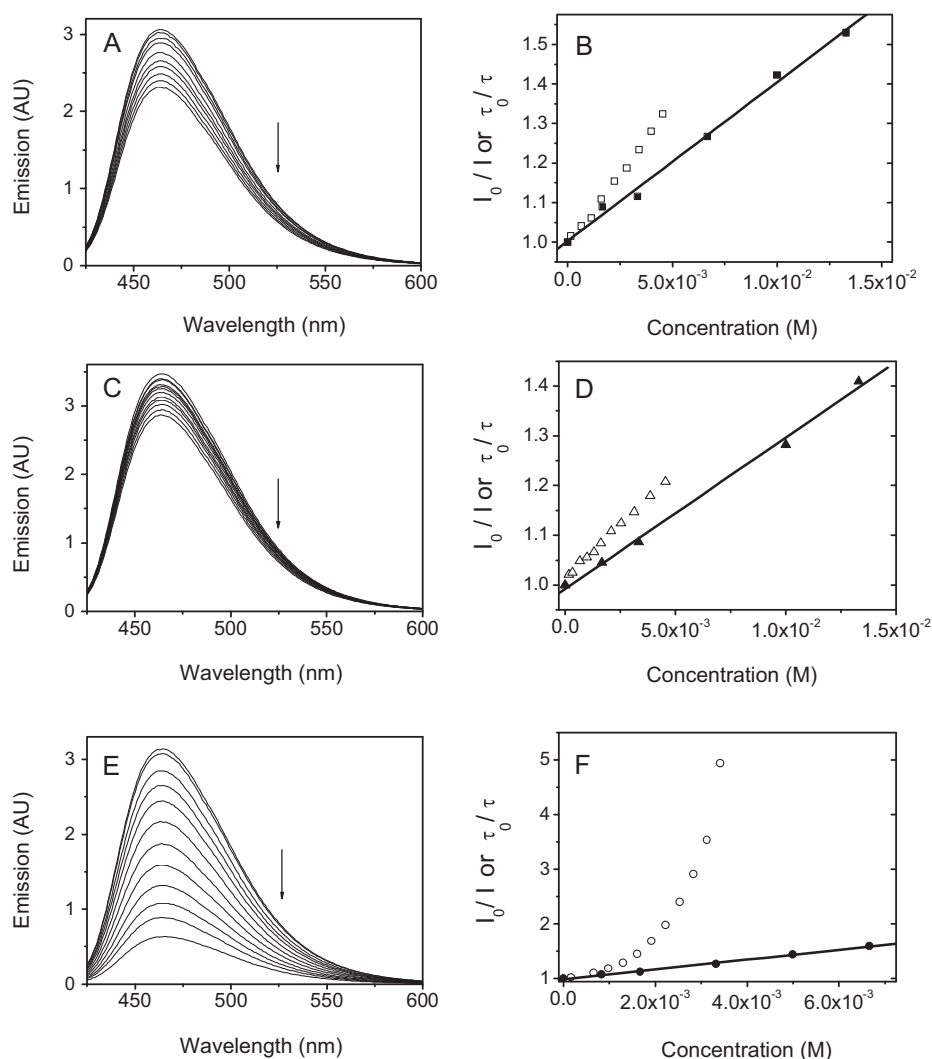
Fig. 4. Fluorescence spectra of TPTP$^+$ in acetonitrile (λ_{exc} = 420 nm) recorded upon addition of increasing concentrations (up to 5×10^{-3} M) of (A) dimethoate, (C) alachlor and (E) pyrimethanil. Stern–Volmer plots of the static (open symbols) and dynamic (solid symbols) quenchings for ($\square$/$\blacksquare$) dimethoate, ($\triangle$/$\blacktriangle$) alachlor and ($\bigcirc$/$\bullet$) pyrimethanil.

between the observed photodegradation and the quenching of the singlet state (Fig. 5). This confirms the active role of the singlet excited state of the photocatalyst in the photooxidation mechanism.
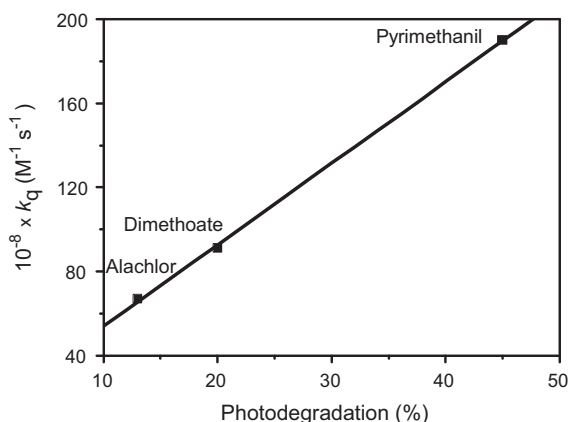

Fig. 5. Relationship between the dynamic quenching constants *versus* the photodegradation percentage for every pollutant.

3.2.2. Transient absorption spectroscopy

To investigate the possible contribution of the triplet excited state of TPTP$^+$ to the photodegradation of the pesticides as an additional mechanistic pathway, laser flash photolysis experiments (LFP) were also carried out. Thus, after excitation (λ_{exc} = 355 nm) of anaerobic acetonitrile solutions of TPTP$^+$, the known broad transient spectrum between 400 and 800 nm, assigned to the triplet-triplet absorption band, was observed [22]. Then, the kinetic evolution of the triplet excited state of TPTP$^+$ (recorded at 470 nm) was monitored in the presence of the pesticides. Interestingly, when identical concentrations of dimethoate, alachlor or pyrimethanil were added (1.6×10^{-4} M), instead of a shortening in the triplet state lifetimes, a moderate (alachlor) to strong (pyrimethanil) decrease in the ΔA, together with the formation of the longer-lived TPTP$^+$ with a broad maximum in the 450–550 region [29], was observed immediately after the laser pulse (Fig. 6A–D). This indicates that the triplet excited state of TPTP$^+$ is not really quenched by the pollutants. Conversely, the decrease in the immediate ΔA supports quenching of shorted-lived precursors, within the duration of the laser pulse.

This hypothesis is consistent with the correlation observed between the transient absorption results and the photodegradation under simulated sunlight. Thus, Fig. 7 shows the relationship between the missing fraction of triplets and the photodegradation
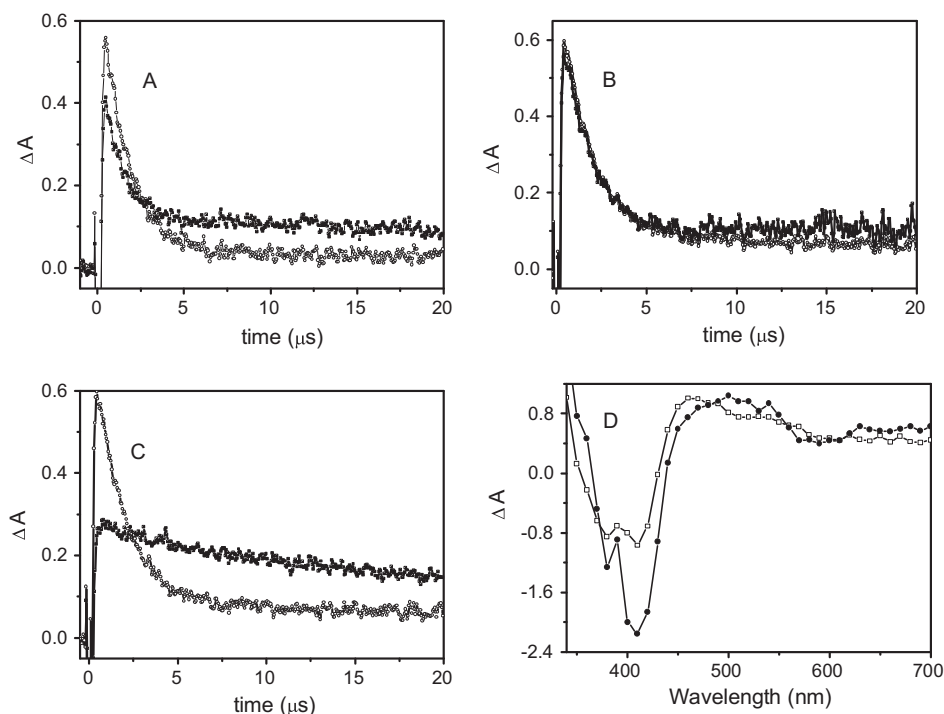
Fig. 6. Decay traces monitored at 470 nm in the absence (○) and in the presence (■) of 1.6×10^{-4} M of: (A) dimethoate, (B) alachlor and (C) pyrimethanil. (D) Normalized transient absorption species recorded 2 μs after LFP ($\lambda = 355$ nm) in deaerated acetonitrile in the absence (□), and in the presence of pyrimethanil (●) (1.6×10^{-4} M).
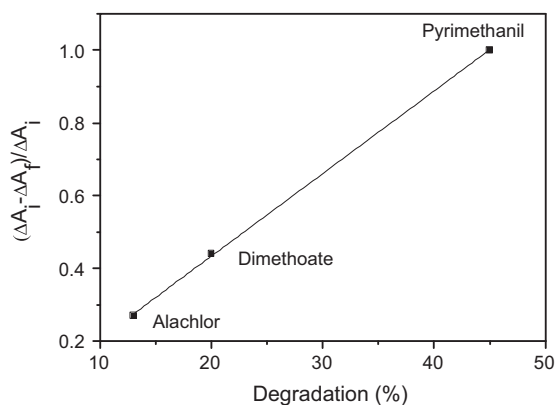

Fig. 7. Relationship between the missing fraction of triplets recorded at 470 nm in the absence and in the presence of the pesticides *vs.* the photodegradation percentage under solar simulated irradiation.

percentage. The former was obtained assuming that the transient observed in the presence of the pesticides is the result of a combination between the signals due to the remaining triplet and the formed radical. In the case of pyrimethanil, no triplet was left, so the signal observed is exclusively due to the TPTP⁺. As the lifetime of

the radical is much longer than that of the triplet, the weight of the two components was easily determined from the decay traces. The missing fraction of triplets is simply defined as the relative decrease of the triplet component immediately after the laser pulse.
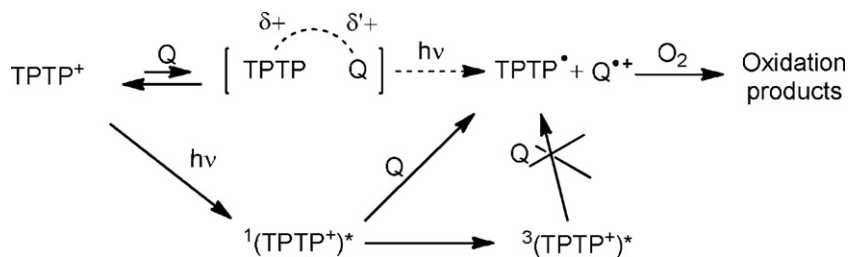
3.3. Electron transfer mechanism

The combined photophysical experimental evidence strongly supports the participation of the singlet excited state, in the photoinduced reaction between TPTP⁺ and the pollutants. Detection of the TPTP⁺, the reduced species derived from the photocatalyst is clearly in favor of an electron transfer mechanism.

Accordingly, calculations using the Rehm–Weller equation (Eq. (2)) [30] indicate that the process is indeed exergonic.

$$\Delta G (\text{kcal mol}^{-1}) = 23.06[E_{\text{ox}}(Q) - E_{\text{red}}(\text{TPTP}^+)] - E^*(\text{TPTP}^+) \quad (2)$$

The values for $E_{\text{red}}(TPTP^+)$ and $E_S^*(\text{TPTP}^+)$ were taken from the literature (-0.21 V *vs.* SCE and 66 kcal mol^{-1}, respectively) [3,31,32]. For the most reactive pollutant (pyrimethanil), the measured $E_{\text{ox}}(Q)$ was $+1.38$ V (*vs.* SCE), the estimated ΔG was -29 kcal mol^{-1}. This indicates that electron transfer from pyrimethanil to the singlet excited state of TPTP⁺ is straightforward. The oxidation potentials of dimethoate and alachlor could not be determined, probably

Scheme 1. Mechanism for the photocatalytic degradation of the pesticides (Q) by TPTP⁺.

because they are ≥ 2 (*vs*. SCE). This justifies their lower reactivity in the solar simulated irradiation.

Overall, the experimental evidence is in agreement with a general mechanism as outline in Scheme 1.

4. Conclusions

Photodegradation of the three pesticides in the presence of TPTP$^+$ as photocatalyst under solar simulated irradiation followed the trend: pyrimethanil > dimethoate > alachlor. An important to moderate steady-state emission decrease, together with a dynamic fluorescence quenching, was observed with quenching constant values of $1.9 \times 10^{10}\,M^{-1}\,s^{-1}$ (pyrimethanil), $9.1 \times 10^{9}\,M^{-1}\,s^{-1}$ (dimethoate) and $6.7 \times 10^{9}\,M^{-1}\,s^{-1}$ (alachlor). In agreement with these results, a decrease in the signal corresponding to the triplet excited state (without any change in the triplet lifetime) was observed immediately after the laser pulse; again a good correlation was observed between the missing fraction of triplets and the photodegradation under solar light. Detection of TPTP$^+$, the reduced species derived from the photocatalyst, as well as Rehm–Weller calculations on the free energy changes, strongly support an electron transfer mechanism occurring from the singlet excited state.

Acknowledgments

References

[1] D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, Chemical Society Reviews 38 (2009) 1999–2011.
[2] M.L. Marin, L. Santos-Juanes, A. Arques, A.M. Amat, M.A. Miranda, Chemical Reviews 112 (2012) 1710–1750.
[3] M.A. Miranda, H. Garcia, Chemical Reviews 94 (1994) 1063–1089.
[4] M.C. DeRosa, R.J. Crutchley, Coordination Chemistry Reviews 233 (2002) 351–371.
[5] N.A. Garcia, F. Amat-Guerri, Chemosphere 59 (2005) 1067–1082.
[6] F. Cermola, N. DellaGreca, M.R. Iesce, S. Montella, A. Pollio, F. Temussi, Chemosphere 55 (2004) 1035–1041.
[7] E. Marais, R. Klein, E. Antunes, T. Nyokong, Journal of Molecular Catalysis A: Chemical 261 (2007) 36–42.
[8] M.A. Miranda, F. Galindo, A.M. Amat, A. Arques, Applied Catalysis B: Environmental 28 (2000) 127–133.
[9] M. Nowakowska, M. Sterzel, S. Zapotoczny, E. Kot, Applied Catalysis B: Environmental 57 (2005) 1–8.
[10] J.P. Escalada, A. Pajares, J. Gianotti, W.A. Massad, S. Bertolotti, F. Amat-Guerri, N.A. Garcia, Chemosphere 65 (2006) 237–244.
[11] A. Arques, A.M. Amat, L. Santos-Juanes, R.F. Vercher, M.L. Marin, M.A. Miranda, Catalysis Today 144 (2009) 106–111.
[12] B. Cojocaru, V.I. Parvulescu, E. Preda, G. Iepure, V. Somoghi, E. Carbonell, M. Alvaro, H. Garcia, Environmental Science and Technology 42 (2008) 4908–4913.
[13] A. Corma, H. Garcia, Chemical Communications (2004) 1443–1459.
[14] A.M. Amat, A. Arques, S.H. Bossmann, A.M. Braun, S. Göb, M.A. Miranda, Angewandte Chemie International Edition 42 (2003) 1653–1655.
[15] A.M. Amat, A. Arques, S.H. Bossmann, A.M. Braun, S. Göb, M.A. Miranda, E. Oliveros, Chemosphere 57 (2004) 1123–1130.
[16] M.A. Miranda, F. Galindo, A.M. Amat, A. Arques, Applied Catalysis B: Environmental 30 (2001) 437–444.
[17] A. Arques, A.M. Amat, L. Santos-Juanes, R.F. Vercher, M.L. Marin, M.A. Miranda, Catalysis Today 129 (2007) 37–42.
[18] M. Alvaro, E. Carbonell, H. Garcia, Applied Catalysis B: Environmental 51 (2004) 195–202.
[19] A. Sanjuan, G. Aguirre, M. Alvaro, H. Garcia, Water Research 34 (2000) 320–326.
[20] M.A. Miranda, A.M. Amat, A. Arques, Catalysis Today 76 (2002) 113–119.
[21] A. Arques, A.M. Amat, L. Santos-Juanes, R.F. Vercher, M.L. Marin, M.A. Miranda, Journal of Molecular Catalysis A: Chemical 271 (2007) 221–226.
[22] M.L. Marin, A. Miguel, L. Santos-Juanes, A. Arques, A.M. Amat, M.A. Miranda, Photochemical & Photobiological Sciences 6 (2007) 848–852.
[23] M.L. Marin, V. Lhiaubet-Vallet, L. Santos-Juanes, J. Soler, J. Gomis, A. Arques, A.M. Amat, M.A. Miranda, Applied Catalysis B: Environmental 103 (2011) 48–53.
[24] R. Wizinger, P. Ulrich, Helvetica Chimica Acta 39 (1956) 207–216.
[25] A. Aguera, E. Almansa, A. Tejedor, A.R. Fernandez-Alba, S. Malato, M.I. Maldonado, Environmental Science and Technology 34 (2000) 1563–1571.
[26] A. Vanni, F. Fontana, Journal of Environmental Monitoring 5 (2003) 635–639.
[27] H.A. Benesi, J.H. Hildebrand, Journal of the American Chemical Society 71 (1949) 2703–2707.
[28] S. Nigam, G. Durocher, Journal of Physical Chemistry 100 (1996) 7135–7142.
[29] S. Marquis, B. Ferrer, M. Alvaro, H. Garcia, H.D. Roth, Journal of Physical Chemistry B 110 (2006) 14956–14960.
[30] D. Rehm, A. Weller, The Israel Journal of Chemistry 8 (1970) 259.
[31] M. Martiny, E. Steckhan, T. Esch, Chemische Berichte-Recueil 126 (1993) 1671–1682.
[32] R. Searle, J.L. Williams, D.E. Demeyer, J.C. Doty, Chemical Communications (1967) 1165.